Natural Analogs for Geologic Sequestration: Cap Rock Evidence for Multi-Million-Year CO₂ Storage

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Naturally occurring carbon dioxide deposits provide unique (but by no means perfect) natural analogs for evaluating the long-term safety and efficacy of storing anthropogenic CO₂ in geologic formations, on a time scale far longer than EOR or underground gas storage activities:

- CO₂ has been trapped for millions of years in those reservoirs with effective cap rocks, such as thick salt or shale deposits. In other settings, CO₂ springs and fluxes developed where cap rocks were breached or faulted.
- Understanding why certain natural geologic settings are effective CO₂ traps while others are not can help guide the screening and designing of engineered sites for CO₂ sequestration. Also, production operations at CO₂ fields provide proven and low-cost technologies applicable to engineered geologic storage sites.

Our study is evaluating three CO₂ fields in the USA that have been effective CO₂ traps for millions of years: the Jackson, McElmo, and St. Johns Domes. Our study has three objectives that are consistent with USDOE's goals for understanding geologic storage and developing long-term, cost-effective verification and monitoring technologies:

- Establish CO₂ Storage as a Natural Process. Studying Natural Analogs documents that CO₂ storage in geologic formations indeed is a natural process. This helps to counter the notion that CO₂ injection is environmentally harmful "waste disposal."
- **Document Long-Term Impacts of CO₂ Storage**. More convincingly than any model or laboratory experiment, Natural Analogs can demonstrate empirically the long-term chemical and physical interactions of CO₂ with reservoir rocks and fluids. Dating the emplacement of CO₂ can uniquely establish the safety and security of geologic storage over very long time periods (thousands to millions of years).
- Assess Surface and Subsurface CO₂ Handling Technologies. Many of the production, monitoring, and safety techniques and facilities developed by the commercial CO₂ production industry can be adapted for long-term geologic storage of CO₂. These technologies and their costs have never been comprehensively documented.

To conduct this study, we have assembled geologic and engineering data from each of the three fields into a GIS data base for mapping and analysis. We also conducted gas sampling for gas composition, and stable and noble gas isotope analysis. Study topics include: geologic setting; CO₂ origin, timing, and storage; cap rock integrity; production operations; and implications for geologic sequestration for each of the three Natural Analog fields. The main results to date include:

- Together, the three study fields stored 2.4 billion t of CO₂, equivalent to more than one year of USA power plant emissions. The fields have been commercially developed for industrial use and offer extensive but largely unexamined data sets on CO₂ reservoir, cap rock and production operations.
- McElmo Dome, the largest field, originally stored 1.6 billion t of supercritical CO₂ within a Carboniferous carbonate reservoir at a depth of 2,300 m. Its cap rock is a 400-m thick sequence of salt (halite) which is finely layered and unperturbed by faults which cut the underlying reservoir; there is no evidence of CO₂ leaking into the overlying strata. Reservoir architecture is complex, with interbedded dolomite (porous,

permeable) and limestone (tight) capped by a significant erosional unconformity. CO_2 concentration is 96-98%, with minor N_2 (1.6-2.2%), CH_4 (0.2-0.9%) and H_2S (0-15 ppm). Trapping is provided by structural closure, permeability barriers in the Leadville, the water/ CO_2 contact, and the salt cap rock. . $\delta 13CO_2$ is uniform (-4.3 to -4.5%), demonstrating no significant internal flow barriers or compartments. The CO_2 likely formed by direct outgassing from Ute Mountain rather than thermal decomposition of the Leadville Limestone (which has $\delta 13CO_2$ of -0.64%). Either origin implies an age of 70 Ma; noble gas analysis in progress should resolve this uncertainty. McElmo Dome has two decades of safe operational history. It currently produces 15 million t/year (800 MMcfd) of 99%-pure CO_2 , which is transported 900 km via pipeline to depleted oil fields for re-injection and enhanced recovery.

- St. Johns Dome contains an estimated 730 million t (13.9 Tcf) of CO₂ which is stored in a free gas state at shallow depth (300-750 m). It is an asymmetrical, faulted anticline located on the southern Colorado Plateau, about 30 km northeast of the Springerville Volcanic Field, a large Plio-Pleistocene (0.3-5 Ma) igneous feature. CO₂ is trapped within the Permian Supai Fm. Overlying and intercalated evaporite deposits (anhydrite, gypsum) and shales act as cap rocks. Supai architecture is complex, with multiple, vertically dispersed reservoirs consisting of sandstone, siltstone, and vuggy dolomite that are separated by thin, impermeable anhydrite seals. CO₂ concentration varies from 83-99%, averaging 92%. Other constituents include nitrogen (6.6%), argon (0.2%), and commercially significant quantities of helium (0.6%). \delta 13CO₂ values were uniform across the field (-3.8%), suggesting that the CO₂ was generated from a single or well-mixed multiple source and that internal barriers and compartmentalization are minimal. CO₂ is widely present (in non-commercial quantities) in the overlying Permian Glorieta Sandstone and San Andres Limestone, entering these formations either by gradual seepage through the cap rock matrix or by overspill and lateral migration, or along fault planes. On the other hand, the presence of helium -- a light and small molecule particularly prone to leakage in high concentrations (up to 1.1%) indicates that the cap rock is sealing over at least the north flank of the field.
- **Jackson Dome** (Pisgah) CO₂ field is a symmetrical, faulted anticline located in the onshore Gulf of Mexico province. CO₂ is trapped within the Jurassic Buckner, Smackover, and Norphlet Fms by structural closure and permeability barriers. Jackson Dome itself is an igneous intrusion of Late Cretaceous age (70 Ma). The Pisgah anticline originally contained an estimated 100 million t (2 Tcf) of CO₂. It is deep (4,700 m) and CO₂ is stored in the supercritical state. Reservoir architecture is complex, with fluvial and eolian sandstones with 8-15% porosity and up to one darcy permeability. CO₂ concentration is 99%, with minor methane, nitrogen and significant H₂S of up to 1%. δ13CO₂ from gas sampled in 10 wells ranges from -3.55 to -2.57 ‰. ³He/⁴He ratios range from 4.27 to 5.01Ra, indicating strong mantle signature. ⁴He/⁴⁰Ar ratios range from 1.26 to 2.52, also indicative of mantle origin. These noble gas isotope data prove that the CO₂ at Pisgah Dome was outgassed from the mantle, rather than derived from thermal decomposition of carbonate. The most likely source was the Jackson Dome intrusion, which is dated to about 70 Ma.

However, the three fields in our study represent but a small sampling of geologic situations. It is not yet possible to define universal criteria for cap rock integrity. Building scientific and public acceptance for geologic CO₂ storage may require that each project have a plausible local or regional natural analog. Future work on Natural Analogs could include: profiling other natural analogs in high-priority sequestration basins located near major anthropogenic CO₂ sources (such as Appalachia, Midwest, etc.); simulating the efficiency and safety of rapid re-filling, including hysteresis effects and tensional stress changes on the cap rock; coring natural CO₂ field cap rocks to determine why they make such excellent seals; soil gas analysis to confirm or disprove cap rock integrity; and developing CO₂-resistant cements designed to withstand exposure for >10,000 years rather than the current time scale of decades.

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